

PAPER • OPEN ACCESS

XPS studies of charging effect induced by X-ray irradiation on amorphous SiO₂ thin films

To cite this article: Dai Peng Xing *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **490** 022079

View the [article online](#) for updates and enhancements.

XPS studies of charging effect induced by X-ray irradiation on amorphous SiO₂ thin films

DaiPeng Xing^{1,*}, HuiZhong Zeng¹, WenXu Zhang¹ and WanLi Zhang¹

¹State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 611731, China

*Corresponding author E-mail: xdpeng1990@163.com

Abstract: X-ray photoelectron spectroscopy has been used to investigate positive charge accumulation on amorphous SiO₂ films induced by in situ X-ray irradiation. We found out two different kinds of samples. The charge accumulation at the surface affects the properties of films. Then, by examining the significant changes of chemical shift and FWHM value, the films show a character of saturation during the process and the results can trace to oxygen vacancies. From the results of loss measured before and after the irradiation, we can say that the performance of highly reflective coatings, especially the surface SiO₂ thin films, will directly affect the gyro abilities.

1. Introduction

Laser gyro inertial navigation system, as one of the core aircraft inertial devices, plays a very important role in many technological fields, and has extensively used for navigation, radar and guidance system. Lockout threshold, which directly affects the precision and stability, is one of the most essential element for gyroscope. However, the lockout threshold depends on the resonant optical path loss mirror, of which the critical component is the high reflection coating where the surface and interfaces plays a key role.[1, 2]

As is known to all, drastic changes in materials properties and performance take place upon the surface charge accumulating.[3] Additional electronic states result from doping or defects, imperfections at their surface and/or the lattice, described as traps, contribute conspicuously to their electrical performance.

Recently, researches in high reflection coatings have been extensively studied in view of the loss, damage caused by laser irradiation and found out the charge accumulation of highly reflective coating, especially at the surface SiO₂ thin films, will directly affect the precision and stability of gyroscope.[4-7] Researches are focusing on the improvement of electrical and optical performance of high reflective coating.



X-ray photoelectron spectroscopy (XPS) commonly used for studying the electronic structure and chemical states of materials. In this paper, we investigated the SiO₂ thin films and the loss of laser gyro. The high reflective coatings irradiated by X-ray and then detected by XPS for several cycles. Furthermore, by examining the changes of the chemical shift and the full width at half maximum (FWHM) value of the O 1s and Si 2p lines, we present the chemical states of Si and O in surface SiO₂ films. Moreover, by studying and comparing the XPS spectra of different times, we try to answer the question whether the surface SiO₂ film plays a primary role in the loss of high reflective coatings.

2. Experiment

The high reflection coating consists of multilayers deposited vertically on a glass-ceramic substrate and a 100 nm thick SiO₂ amorphous thin film covers the surface. XPS spectra were measured by using a Kratos Axis spectrometer with monochromatic Al K α (1486.71 eV) X-ray radiation with a base pressure of 1×10^{-8} Pa.

In order to imitate the working environment of laser irradiation in gyroscope, which may cause positive charge accumulating on the surface of high reflection coating, we exposed the high reflection films to X-ray before the detection of photoelectron spectroscopy when Low Energy Electron Neutralizer began to work. The irradiation was in situ performed, and we kept it on throughout the experiment while detected the structure of surface every five minutes for five cycles.

XPS survey spectra (100–1500 eV) on the pristine film was firstly measured before the high-resolution scan of C 1s, Si 2p and O 1s. Elements Si, O and C all can be obviously found in the survey spectrum. The Si 2p and O 1s high-resolution spectra calibrated by the peak of C 1s with a standard binding energy of 284.8 eV. It is necessary to establish suitable peak fitting procedure by extracting further particulars of chemical states information from the high-resolution spectra. Gaussian-Lorentzian line shapes (GL30), here, used for fitting the Si 2p and O 1s spectra after conventional Shirley background subtraction. Meanwhile, we ignored the splitting of Si 2p peaks from amorphous SiO₂ film.

3. Result and Discussion

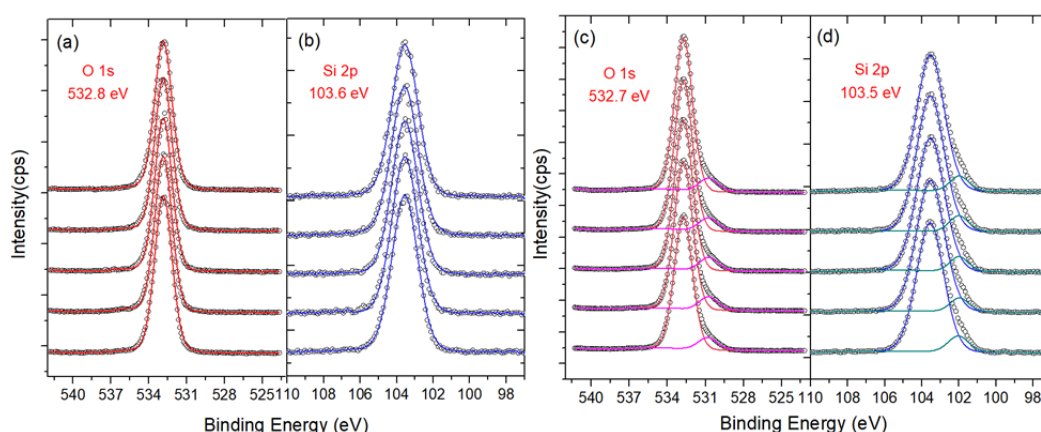


Figure 1: XPS spectra of O 1s and Si 2p core level for SiO₂ film under X-ray irradiation, each sample is detected for five times. The deconvolution fits the raw peak (open circle) with full lines, figure (a), (c) are for sample 1, 2, respectively. The figure shows the chemical states and shifts and their variation upon times.

Figure 1 shows typical high-resolution XPS data with deconvolution fit peaks for both Si 2p and O 1s spectra. It is worthy to notice that there are two significant types of spectrum, one can be fitted with only a symmetric peak while the other shows a shoulder with an energy shift to lower binding energy. Therefore, it demonstrates that the structure of SiO₂ film is different under X-ray irradiation.

For Si 2p spectra, the only one chemical structure corresponding to the Si oxidation state Si⁴⁺ clearly observed at binding energy of 103.5eV, similar to the reported works, see figure 1(b).[8-10] However, by deconvoluting the spectra, an unchangeable predominant peak and a shoulder with an energy shift from 103.5 to 102.0eV can be found obviously in sample 2, see figure 1(d). It is reasonable to attribute to the Si oxidation state Si³⁺. [3] This is consistent with the observation from. [9,10] On the other hand, we can find out the same features in O 1s spectra, one peak for sample 1 is located at 532.9eV, while O 1s spectrum exhibits two contributions in sample 2 and the shoulder is account for oxygen vacancies. Another interesting finding is that the predominant peaks for all samples have not changed during the irradiation.

We can see that the shoulders located at lower binding energy changes a little and the chemical shifts become stable with the irradiation time increasing. The shifts of the binding energy for sample 2 is proposed to be caused by the accumulation of positive charges near the surface, where photoelectrons are emitted with a kinetic energy leaving positive charges behind. Which is similar to the work environment of high reflection coating in laser gyro.

It has been reported that the chemical shift is affected by the local electrical potential resulting from positive charge accumulation. In this work, the C 1s core level binding energy due to surface contamination was used to calibrate and monitor the charging effect. However, there is no significant change by comparing the measured spectra of C 1s during the irradiation. Thus, we can assume that at the beginning of the irradiation the surface is unstable (contaminants, defects, charge traps) and can be affected immediately with the accumulation of charge.[11]

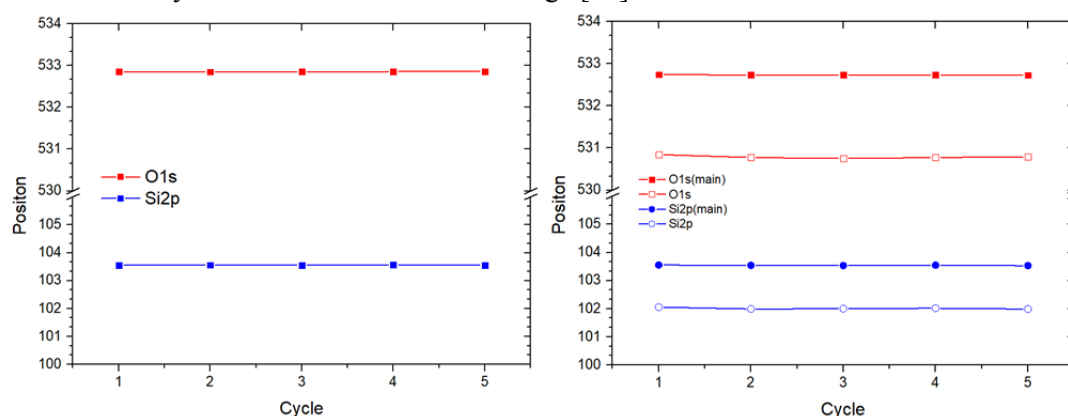


Figure 2: Peak position evolution of the chemical structures as a function of irradiation process.

Figure 2 summarizes the binding energy shifts measured with respect to Si 2p and O 1s as a function of irradiation time. We can see that an unchangeable predominant peak in the binding energy shift for both samples and the shoulder located at lower binding energy changes a little, where the chemical shifts become larger and stable with the irradiation time increasing.

In general, when a sample exposes to the X-ray, the surface is irradiated by photons with characteristic energy, and these photons directly interact with core electrons of atoms near the surface.[12] Then, photoelectrons emitted with a kinetic energy leaving positive charges behind.

Which is similar to the work environment of high reflection coatings in laser gyro. The positive charges accumulation result from electron emission and multiple inner relaxation. Such processes are fast comparing with the XPS measurements. However, the process of charge capturing by various kinds of structure traps for example oxygen vacancies can be much longer.[12] Therefore, we can suppose that the charge accumulation, in this work, mainly derives from the oxygen vacancies and further influence the electronic states of film.

It has been known that the binding energy shift is affected by the local electrical potential due to charge accumulation and application of external voltage bias to non-conducting samples introducing additional charging shifts.[11] In this work, the C 1s core level binding energy result from surface contamination was used to calibrate and monitor the charging effect. Moreover, there is no significant change by comparing the measured spectra of C 1s during the irradiation.

Thus, we can assert that at the beginning of the irradiation the surface is unstable (contaminants, defects, charge traps) and can be effected immediately with the accumulation of charge. With the increasing of irradiation time, the charge accumulation is saturated and the surface environment become more stable due to charge distribution and chemical reconstruction, which result in the saturation of chemical states.

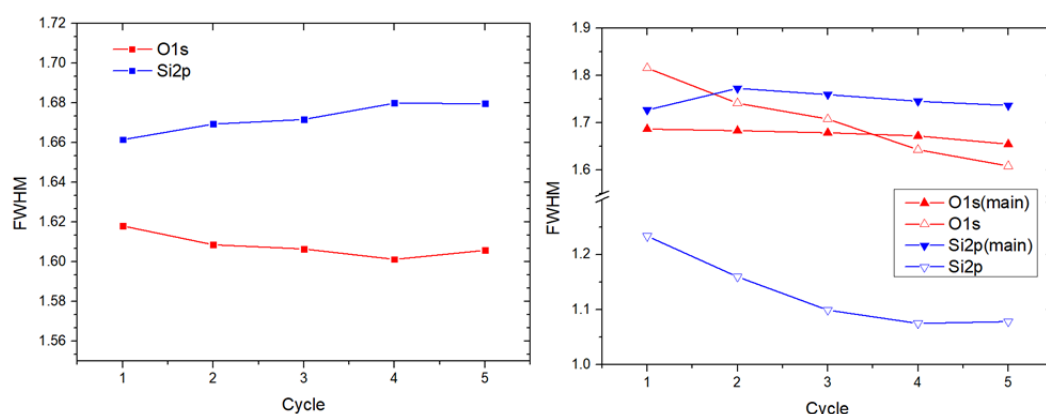


Figure 3. FWHM evolution of the chemical structures as a function of irradiation time.

Figure 3 depicts that the FWHM depend on the X-ray irradiation process. For both samples, the O1s predominant peaks become narrow and the FWHM value decreases slowly while the Si2p peaks become border and then keep stable and decrease slowly for sample 1 and 2, respectively. It is noteworthy that FWHM values change less than 0.02eV for sample 1, and keep the values for Si 2p and O 1s between 1.6~1.7eV. Moreover, it is worth to notice that, for sample 2, the FWHM value of Si 2p shoulder is much less than the predominant peak and O1s peaks. The peaks always keep becoming narrow and the FWHM value decreases quickly and then keeps stable during the irradiation, showing a character of saturation, which indicates a good agreement with the change of chemical shift. Generally, the linewidth will become border with charging accumulation.[13] However, during the processing of irradiation, charge distribution and chemical reconstruction, the high reflection coating become more complicated and the FWHM values show an unusual change.

Table I shows the comparison of loss before and after irradiation. As expected, the loss of sample 2 with more defects (oxygen vacancies) increased apparently while the other kept nearly the same.

Table 1. Loss of high reflection coatings before and after irradiation

Sample	Loss (ppm)	
	Before	After
1	112	115
2	114	164

4. Conclusion

In summary, the surface chemical states of amorphous SiO₂ thin films as high reflection coatings were studied by XPS. Using in situ X-ray irradiation, we imitate the working environment of laser irradiation in gyroscope, positive charge accumulating took place near the surface of high reflection coating, and the charges accumulation affects the film properties of chemical shift and FWHM value. There are two kinds of samples shows different changes of XPS spectra. One kind shows no obvious changes during irradiation, while the other kind shows significant evolution of chemical shift and FWHM value. Furthermore, it is important to highlight that both samples show the character of saturation with the increasing of irradiation time. From the loss measured before and after the irradiation, we can say that the performance of highly reflective coating, especially the surface SiO₂ thin films, will directly affect the gyro abilities.

Acknowledgements

This work was financially supported by the National Natural Science Foundation (U1435208, 51672035, 51602039).

References

- [1] M.Q. Zhan, Enhancement of the LIDT of Optical Coatings, Journal of Shanghai Second Polytechnic University, (2010).
- [2] P. Baumeister, Dependence of the reflectance of a multilayer reflector on the thickness of the outer layer, Applied Optics, 38 (1999) 6034-6035.
- [3] J.H.S. Annett Thøgersen, and Erik S. Marstein, Oxidation effects on graded porous silicon anti-reflection coatings, Journal of the Electrochemical Society, (2012).
- [4] S. Jena, R.B. Tokas, S. Thakur, N.K. Sahoo, Influence of annealing on optical, microstructural and laser induced damage properties of TiO₂/SiO₂ multilayer high reflection mirror, in: American Institute of Physics Conference Series, 2017, pp. 4356-4364.
- [5] G.J. Exarhos, H. Qi, A.H. Guenther, K. Yi, H. Yu, K.L. Lewis, D. Ristau, Y. Cui, D. Li, M.J. Soileau, C.J. Stolz, Z. Gao, J. Shao, Z. Fan, Laser-induced damage of multilayer high-reflectance coatings for 248 nm, in: Laser-Induced Damage in Optical Materials: 2007, 2007.
- [6] S. Xu, X. Zu, X. Jiang, X. Yuan, J. Huang, H. Wang, H. Lv, W. Zheng, The damage mechanisms of fused silica irradiated by 355nm laser in vacuum, Nuclear Instruments & Methods in Physics Research, 266 (2008) 2936-2940.
- [7] J. Xu, C. Chen, T. Zhang, Z. Han, A Study of Polycrystalline Silicon Damage Features Based on Nanosecond Pulse Laser Irradiation with Different Wavelength Effects, Materials, 10 (2017) 260.
- [8] Z.Y. Lu, C.J. Nicklaw, D.M. Fleetwood, R.D. Schrimpf, S.T. Pantelides, Structure, properties, and dynamics of oxygen vacancies in amorphous SiO₂, Phys Rev Lett, 89 (2002) 285505.
- [9] Y. Liu, Y.Q. Fu, T.P. Chen, M.S. Tse, S. Fung, J.-H. Hsieh, X.H. Yang, Depth Profiling of Si

- Oxidation States in Si-Implanted SiO₂ Films by X-Ray Photoelectron Spectroscopy, Japanese Journal of Applied Physics, 42 (2003) L1394-L1396.
- [10] K.J. Kim, J.W. Kim, M.-S. Yang, J.H. Shin, Oxidation of Si during the growth of SiO_x by ion-beam sputter deposition: In situ x-ray photoelectron spectroscopy as a function of oxygen partial pressure and deposition temperature, Physical Review B, 74 (2006).
- [11] T.P.C. Y. Liu, L. Ding, S. Zhang, Y. Q. Fu and S. Fung, Charging mechanism in a SiO₂ matrix embedded with Si nanocrystals.pdf, J. Appl. Phys, (2006).
- [12] Y.Y. Lebedinskii, A.G. Chernikova, A.M. Markeev, D.S. Kuzmichev, Effect of dielectric stoichiometry and interface chemical state on band alignment between tantalum oxide and platinum, Applied Physics Letters, 107 (2015).
- [13] G.M. Bancroft, H.W. Nesbitt, R. Ho, D.M. Shaw, J.S. Tse, M.C. Biesinger, Toward a comprehensive understanding of solid-state core-level XPS linewidths: Experimental and theoretical studies on the Si 2p and O 1s linewidths in silicates, Physical Review B, 80 (2009).